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Sodium alginate/Na$^+$-rectorite composite microspheres: Preparation, characterization, and dye adsorption

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ABSTRACT

Sodium alginate/Na$^+$-rectorite (SA/Na$^+$REC) intercalated nano-composite microspheres were prepared in an inverse suspension system. The effect of the preparation conditions of SA/Na$^+$REC composite microspheres on adsorption capacity for Basic Blue 9 was investigated. The structure and morphology were analyzed by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The results showed that the optimal condition was that the amount of Na$^+$-rectorite was 2 wt%, the amount of cross-linker was 0.384% and the amount of the initiator was 8%. SEM showed that it is porous products with spherical particulate surface. XRD showed that intercalation is formed between Na$^+$-rectorite and sodium alginate.

The adsorption capacity of SA/Na$^+$REC was investigated in comparison with Na$^+$-rectorite and sodium alginate using different cationic dyes. The SA/Na$^+$REC composite microspheres showed the highest adsorption capacity. The reason lies in the existence of intercalated sodium alginate. It could enlarge the pore structure of microspheres, facilitating the penetration of macromolecular dyes.

1. Introduction

Organic dye effluent is one of the most important water pollution problems in various industries such as textile, paper, plastic, leather, food, and cosmetic (Meysam, Rozaimah, Abdullah, & Hosseini, 2011; Mohamad, Dalia, Wan, & Azni, 2011). The most important characteristic of these organic dyes is that they are nondegradable and thereby they are persistent in the environment. Therefore, the elimination of organic dye from water and wastewater is important to protect environment and public health (Gurusamy, Lai, & Lee, 2008; Meysam et al., 2011). Various methods of dye removal have been studied and developed including physical, chemical, physico-chemical and biological methods (Burkinshaw & Kabambe, 2009; Gupta & Suhas, 2009). Adsorption is considered as an economical and efficient method for dye removal. Various kinds of competent adsorbents have been reported such as activated carbon (Meysam et al., 2011; Yenisoy-Karakaş, Aygün, Güneş, & Tahtasakal, 2004), natural and synthetic zeolites (Teli, Gokavi, & Aminabhavi, 2007; Wang, Li, Wang, Sun, & Huang, 2009) and resins (Lin & Juang, 2009; Yenisoy-Karakaş et al., 2004). Although resins have large organic matters absorbing capacities, those prepared from natural polysaccharides have been purposed and developed for dye removal due to their low cost, bio-degradability and friend-environmental nature, such as starch (Zhao, Li, Wang, & La, 2008), chitosan (Gurusamy et al., 2008; Syed, Muhammad, & Allah, 2011; Wang, Du, Luo, Lin, & Kennedy, 2007) and chitin (Gülbahar, Uzun, & Güzel, 2007).

Sodium alginate is a kind of polysaccharide in nature, which is mainly composed of (1–4)-linked β-D-mannuronic acid units and α-L-guluronic acid units (Teli et al., 2007). The gel forming property, biocompatibility, nontoxicity and biodegradability of sodium alginate suggest it would have application prospects, as medical materials, sanitary materials, tissue engineering materials, controlled-release devices, and matrices for enzyme immobilization, etc. (Smitha, Sridha, & Khan, 2005; Tuncer, Demircia, Eroglub, & Olgun, 2005). Sodium alginate has been used as adsorbent (Annadura, Ruey-Shin, & Duu-Jong, 2002; Mouloud, Jean-Philippe, Michel, & Omar, 2010; Rathinam, Nishtar, Jonnalagadda, & Balachandran, 2007).

Rectorite, another type of layered material having similar structure with montmorillonite and being easily available in China, exhibits good mechanical, thermal properties, adsorption properties and high resistance to ultraviolet ray, etc. (Toshio, Ikumi, Yuko, & Rumiko, 2005). Rectorite has been reported as adsorbent. Zhang et al. (2005) studied the adsorption of Cu(II) and Zn(II) on rectorite and found that the adsorption quickly reach equilibrium. Huang, Ma, Liang, and Yan (2005) studied the adsorption of phenol on organic-modified rectorite and found that organic-modified

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rectorite is a suitable candidate for preconcentration of phenol. However, little information concerned polysaccharides/rectorite composite adsorbent.

In this study, a new type of crosslinked sodium alginate/Na^+-rectorite intercalated nano-composite microspheres (SA/Na^+REC) were synthesized in an inverse suspension system with sodium alginate and Na^+-rectorite as raw materials, N,N′-methylene bisacrylamide as a crosslinker, and kalium persulphate as an initiator. The structure and morphology of SA/Na^+REC composite microsphere were studied with FTIR, XRD and SEM. The adsorption properties of SA/Na^+REC composite microsphere were researched with several cationic dyes.

2. Experimental

2.1. Materials

The materials included sodium alginate (SA) [analytical reagent (AR), Kemiou Chemical Co. Ltd. (Tianjing, China)], rectorite (REC) [Hubei Zhongxiang Rectorite Mine (Wuhan, China)], cyclohexane, chloroform, sodium hydroxide, kalium persulphate ($K_2S_2O_8$, KPS), ethyl acetate, acetone, anhydrous ethanol [AR, Tianjin Damao Chemical Reagent Factory (Tianjin, China)], Span60 [AR, Shanghai Yuanji Chemical, Ltd. (Shenyang, China)], sodium pyrophate [AR, Tianjin Boddy Chemical Co., Ltd. (Tianjin, China)], glycerine [AR, Tianjin Daqiuzhuang Froth Plastics Plant (Tianjin, China)], Tween60 [AR, Beijing Qingshengda Chemical Co., Ltd. (Beijing, China)], and N,N′-methylene bisacrylamide (NMBA) [AR, Beijing Hengyezhongyuan Chemical Co., Ltd. (Beijing, China)]. Basic Blue 3, Basic Blue 9, Basic Blue 54, Basic Yellow 1 and Basic red GTL [AR, Rugao Wu Xing Chemical Co., Ltd. (Rugao, China)].

2.2. Synthesis of Na^+REC

Rectorite was calcined in 850 °C for 4 h to increase its white degree and improve its activity (Castelein, Soulestin, & Bonnet, 2001). Then calcined rectorite was treated with sodium pyrophate in order to intensify insertion effect of sodium alginate. The synthesis of Na^+-rectorite was performed as following steps. Firstly, 10.0 g of calcined rectorite was dissolved in deionized water to obtain 15 wt% suspending solution. Secondly, 0.3 g sodium pyrophate was added into the suspending solution with stirring and maintained at the condition for 0.5 h to obtain a mixture. Thirdly, the mixture was slowly heated to 60 °C and maintained at that temperature for 12 h. Fourthly, the mixture was cooled to 30 °C, then it was filtered on a Buncher filter and dried. The product is coded as Na^+REC.

2.3. Synthesis of SA/Na^+REC intercalated nano-composite microspheres

Na^+REC was dissolved in deionized water to obtain 3 wt% suspending liquid through ultrasonic dispersion for 10 min. Sodium alginate was dissolved in deionized water to form a homogeneous solution of 3 wt% polysaccharide. The sodium alginate solution was slowly mixed into Na^+REC suspending liquid, then glycerine (10% (w/w) based on SA) as the plasticizer was dropped into the mixture. The mixture was stirred with a high speed shear mixer for 3 h. Cyclohexane (80 mL) and chloroform (20 mL) were placed in a three-necked flask and heated with a water bath to 60 °C under conditions of reflux. Span60–Tween60 (1 g) as an emulsifier was added. The water phase was added to the oil phase while the mixture was stirred. After the oxygen was ejected completely from the three-necked flask by a nitrogen flow, N,N′-methylene bisacrylamide and kalium persulphate were added. The crosslinking reaction was carried out for 2 h at a temperature of 80 °C. The reaction solution was removed and separated by centrifugation. The underlayer crosslinked polymers were subsequently washed with ethyl acetate, acetone, and anhydrous ethanol. Then, they were dried, and a white or pale yellow SA/Na^+REC powder was obtained.

2.4. Measurements

FTIR spectra of sodium alginate, Na^+REC and SA/Na^+REC composite were recorded with potassium bromide pellets on a Fourier Transform Infrared Spectrometer (Model VECTOR-22, Shimazu, Kyoto, Japan).

The structures of sodium alginate, Na^+REC and SA/Na^+REC composite were investigated using DPmax23C X-ray diffraction (XRD) instrument (Rigaku, Osaka, Japan) with Cu K_α ($\lambda = 0.154$ nm) radiation source. The X-ray generator operated at 35 kV and 50 mA, the reflection angle 2θ was monitored from 2.0° to 30° at a scanning speed of 2°/min and a step size of 0.02°.

The morphology of product was observed using scanning electron microscopy (KYKY1000B, Scientific Instrument Factory Chinese Academy of Sciences, Beijing, China). Prior to observation, sample was arranged on metal grids by using double-sided adhesive tape, in addition, sample was coated with gold under vacuum.

The adsorption experiment was carried out in 250-mL Erlenmeyer flasks equipped with stoppers, in which 0.1000 g absorbent, i.e. Na^+REC, sodium alginate or SA/Na^+REC composite microspheres and 100 mL aqueous dye solutions with an initial concentration of 500 mg/L. The mixtures were vigorously stirred for 12 h at 298 K. The dye solutions were separated from the adsorbents by centrifugation at 3500 rpm for10 min. The absorbency of the solutions was determined with a UV–visible spectrophotometer (UV-265FW, Shimadzu Corp. (Kyoto, Japan)) at $\lambda = 655$ nm. The adsorpcy (mg/g) and removal (%) were calculated according to Eqs. (1) and (2), respectively:

$$\text{Adsorpcy} = \frac{V(c_0 - c_1)}{m} \tag{1}$$

$$\text{Removal} = \frac{c_0 - c_1}{c_0} \tag{2}$$

where c_0 is the initial solution concentration (mg/L), c_1 is the final solution concentration (mg/L), V is the solution volume (L), and m is the mass of the absorbent (g).

3. Results and discussion

3.1. Mechanism of synthesis of SA/Na^+REC composite microspheres

SA/Na^+REC intercalated nano-composite was prepared via a solution-mixing processing technique. Rectorite is a type of layered materials and its thickness of a single rectorite layer is about 2 nm. The swellable silicate layers of Na^+REC are exfoliated into sodium alginate matrix depends on two processes, namely, sodium alginate chain intercalation into clay galleries, and nano clay layers exfoliation under shearing force. The sum of van der Waals force and electrostatic attractive force against clay exfoliation, while the shearing force and elastic force arising due to sodium alginate molecular intercalation favor clay exfoliation (Pathavuth and Punnama, 2009; Yang, Liang, Zhang, He, & Wang, 2009). There is a strong intermolecular hydrogen bonding interface between active hydroxyl on the surface of Na^+REC and carboxyl of sodium alginate.

The mechanism for preparation of crosslinked SA/Na^+REC composite microspheres in an inverse suspension system is showed in Fig. 1. Preparation includes chain initiation and crosslinking. Peroxysulfate ion serves as a thermally dissociated initiator; it is readily dissociated to $SO_4^{-\bullet}$ and then the radicals abstract hydrogen from the hydroxyl groups in the sodium alginate chain to form

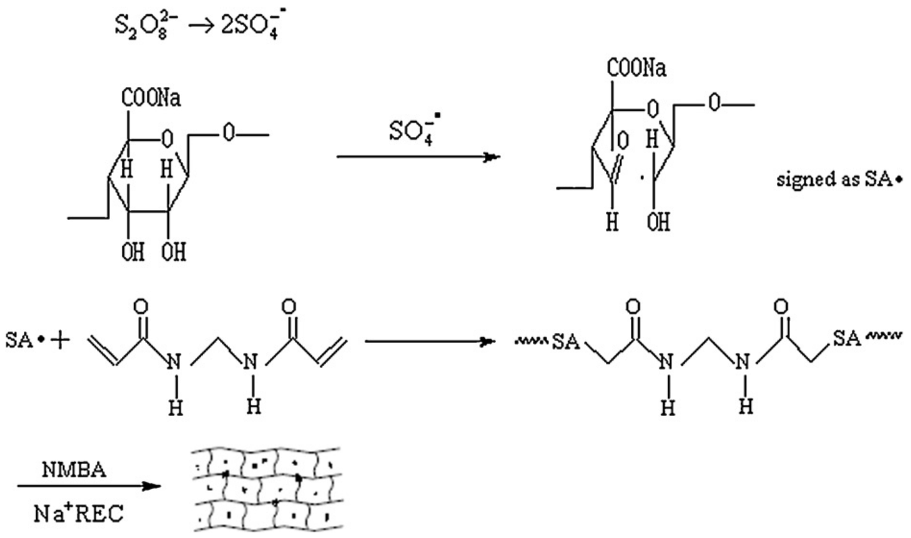

Fig. 1. Scheme of synthesis of crosslinked SA/Na$^+$REC composite microspheres.

corresponding alkoxy radicals on the substrates. N,N′-methylene bisacrylamide has two double bonds that can contribute to the crosslinking reaction. The cross-linking formation can be carried out in two ways: (a) the alkoxy radicals on the sodium alginate backbones result in active centers capable of initiating free radical reactions with N,N′-methylene bisacrylamide; (b) self-crosslinking of the free radicals onto sodium alginate results in crosslink points (Pourjavadi, Barzegar, & Mahdavinia, 2006). At the same time Na$^+$REC clay mineral particle in network acted as crosslinking point, which caused the formation of an additional network. After the processes of chain crosslinking, the crosslinked SA/Na$^+$REC composite microspheres were obtained.

3.2. *Effects of Na$^+$REC, kalium persulphate and N,N′-methylene bisacrylamide contents on adsorption*

Fig. 2a–c shows the influence of Na$^+$REC, kalium persulphate and N,N′-methylene bisacrylamide contents on adsorption capacity of SA/Na$^+$REC composite microspheres. As can be seen from Fig. 2a, the adsorption capacity of SA/Na$^+$REC composite microspheres increased from 371 mg/g to 493 mg/g, as 2 wt% Na$^+$REC (based on sodium alginate) was introduced. But the adsorption capacities of the SA/Na$^+$REC composite microspheres decrease with further increasing Na$^+$REC content. The reason lies in the low concentration of Na$^+$REC resulted in the existence of intercalate sodium alginate (Wu, Wei, Lin, & Lin, 2003; Yang et al., 2009). It could enlarge the pore structure of SA/Na$^+$REC, facilitating the penetration of macromolecular dyes, and also electrostatically interact with the applied dyes. However, the interaction among Na$^+$REC and sodium alginate became intensive gradually at higher Na$^+$REC content. In addition, superfluous Na$^+$REC clay mineral particle in network acted as crosslinking point, so more chemical and physical crosslinkages were formed in the polymeric network, and then elasticity of the polymer chains decreases, which decreased adsorption capacity of SA/Na$^+$REC.

Kalium persulphate was used as the initiator in the preparation. Fig. 2b shows the effect of kalium persulphate amount on adsorption. Initially, more content of kalium persulphate leads to high adsorption capacitie of SA/Na$^+$REC composite, but when the kalium persulphate content is higher than 8 wt%, the adsorption capacitie declines. This could be explained by the fact that the initiator is mostly utilized in producing a large number of free-radical sites on sodium alginate. When the kalium persulphate content

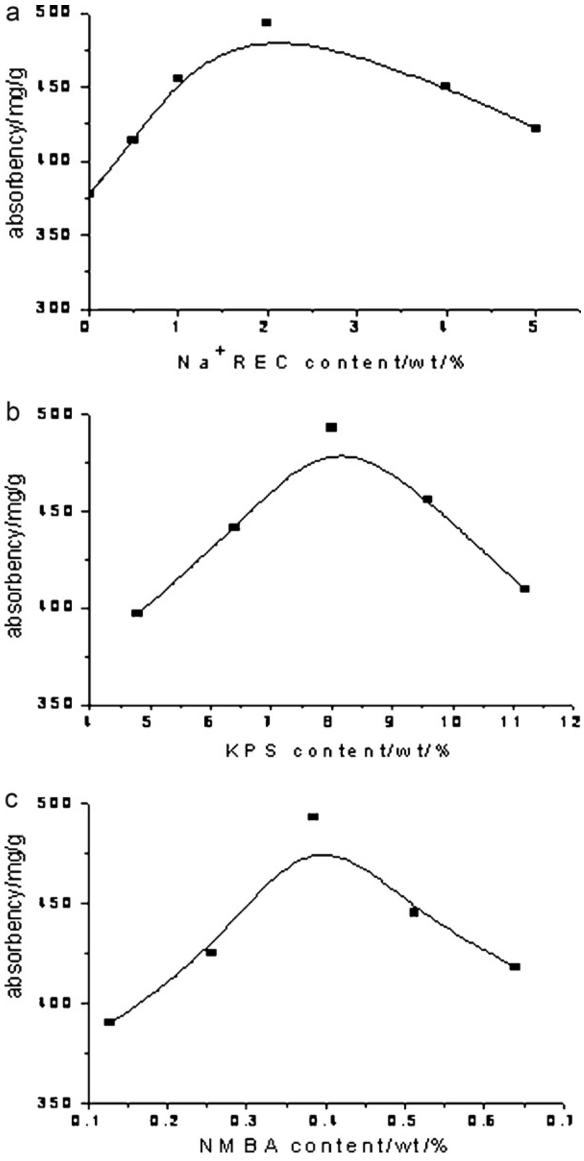

Fig. 2. Effects of Na$^+$REC, kalium persulphate and N,N′-methylene bisacrylamide contents on adsorption.

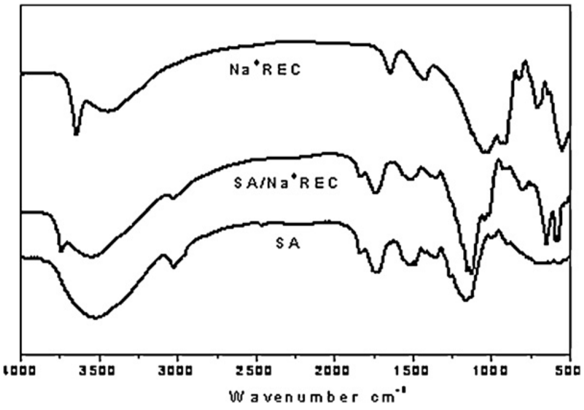

Fig. 3. FTIR spectra of Na$^+$REC, sodium alginate and SA/Na$^+$REC.

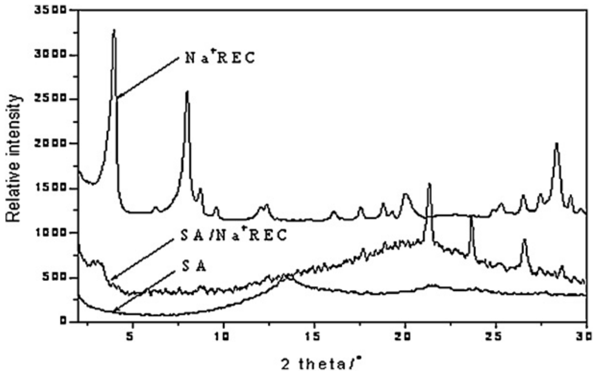

Fig. 5. X-ray diffraction patterns of Na$^+$REC, sodium alginate and SA/Na$^+$REC.

increases, the system produce more active center and the degree of crosslinking increased rapidly. However, continuous increase of the kalium persulphate content leads to faster increase of homopolymerization rate of crosslinker, and thus the decrease of the degree of crosslinking.

The effect of the amount of N,N′-methylene bisacrylamide on adsorption capacities, which was used as the cross-linker in the preparation, was studied and the result was shown in Fig. 2c. When the crosslinking agent dosage was lower than 0.384 wt%, the adsorption capacity for Basic Blue 9 increased with the rising ratio; however it began to decrease with the increasing cross-linker content when it was higher than 0.384 wt%. The reason lies in low concentration of the cross-linker leads to low degree of cross linking, and it is hard for network structure to form, so the adsorption capacities for Basic Blue 9 is low (Wang, Zhang, & Wang, 2008; Zhao et al., 2008). However, when it is higher than 0.384 wt%, there are more cross-linking points and the pores become smaller in the network, which causes the macroscopic decrease of the absorbency.

So the optimal condition was that the content of Na$^+$REC was 2 wt%, the content of kalium persulphate was 8% and the content of N,N′-methylene bisacrylamide was 0.384%.

3.3. Structure and morphology of SA/Na$^+$REC composite microspheres

Fig. 3 shows the comparative FTIR spectrograms of Na$^+$REC, sodium alginate and SA/Na$^+$REC composite microspheres. For Na$^+$REC, 3431 cm^{-1} is attributed to the bending vibration of hydrogen band of interlaminar water, 3632 cm^{-1} is attributed to the hydroxyl stretching of SiOH, 1050 cm^{-1} is associated with the anisomerous stretching vibration of Si—O—Si, 550 cm^{-1} is attributed to the bending vibration of Si—O (Pathavuth and Punnama, 2009; Yang et al., 2009). The FTIR spectrum of sodium alginate showed absorption bands at 3493 cm^{-1} (OH stretching), 1618 cm^{-1} (COO$^-$ asymmetric stretching), and 1421 cm^{-1} (COO$^-$ symmetric stretching). The FTIR spectrum of the SA/Na$^+$REC composite shows the combination of characteristic absorptions due to the sodium alginate and Na$^+$REC groups. The peak at 3632 cm^{-1} (OH stretching vibration of SiOH of Na$^+$REC) and 3493 cm^{-1} (OH stretching vibration of sodium alginate) shifted to high wavenumber, indicating that the hydroxyl group existed before and after the crosslinking reaction, but the production of SA/Na$^+$REC composite weakened the association between hydrogen bonds (Pourjavadi et al., 2006; Zhao et al., 2008). The peak at 1652 cm^{-1} of carbonyl group in the sodium alginate was shifted to 1620 cm^{-1} in SA/Na$^+$REC spectrum, indicating that a certain degree of intermolecular interactions between sodium alginate and Na$^+$REC existed due to the intercalation. A new and weak peak appeared at 1538 cm^{-1} that attributed to the presence of amide group of N,N′-methylene bisacrylamide in SA/Na$^+$REC composite microspheres (Zhao et al., 2008). Thus, we deduced that apparently, a crosslinking reaction took place between sodium alginate and N,N′-methylene bisacrylamide.

As shown in Fig. 4a, the synthesized SA/Na$^+$REC composite in an inverse suspension system were spherical particulates and the average diameter was about 18.2 μm (analyzed with a particle size analyzer). It can be also seen from Fig. 4b that SA/Na$^+$REC composite microsphere exhibits loose structure, which lead to high the absorption for Basic Blue 9.

Fig. 5 displays the analysis results of XRD of Na$^+$REC, sodium alginate and SA/Na$^+$REC composite microsphere. Pure sodium alginate has an amorphous morphology. The XRD pattern of the Na$^+$REC shows a reflection peak at about $2\theta = 4.0^\circ$, corresponding to a basal spacing (d_{001}) of 2.2073 nm. It can be observed from Fig. 5 that the (0 0 1) plane diffraction peaks of SA/Na$^+$REC composites are shifted to low angle and have weaker (0 0 1) plane reflection peaks than

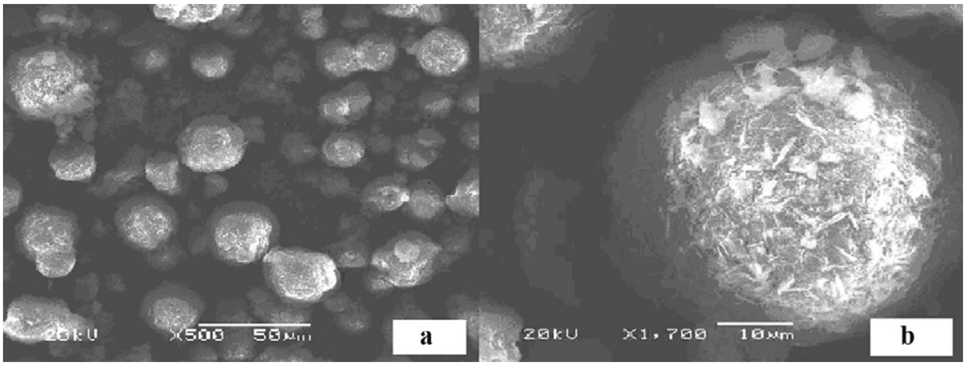

Fig. 4. SEM photographs of SA/Na$^+$REC composite microsphere.

Table 1
Cationic dye adsorption of sodium alginate, Na^{+}REC and A/Na^{+}REC composite microspheres.

Dye	Removal (wt%)			Absorbency (mg/g)		
	Na^{+}REC	SA	SA/Na^{+}REC	Na^{+}REC	SA	SA/Na^{+}REC
Basic Blue 3	61	68	96	307	339	482
Basic Blue 9	69	74	99	343	371	493
Basic Blue 54	47	51	78	237	254	388
Basic Yellow 1	56	61	93	278	307	467
Basic red GTL	53	59	89	265	297	443

Na^{+}REC. According to the Bragg's law, the d_{001} values of SA/Na^{+}REC composites are larger than Na^{+}REC, indicating that intercalation is formed between Na^{+}REC and sodium alginate.

3.4. Dye adsorption

Dye adsorption of sodium alginate, Na^{+}REC and SA/Na^{+}REC composite microspheres are investigated and results are listed in Table 1. The Na^{+}REC showed the lowest adsorption capacities for these five basic dyes. The adsorption of Na^{+}REC was mainly due to cation exchange with the dye cations (Pathavuth and Punnama, 2009). The adsorption of SA/Na^{+}REC was significantly higher than that of Na^{+}REC and sodium alginate. This increase resulted from the synergistic effect of broadened pores and electrostatic interaction between intercalated sodium alginate and the dyes. The larger pores of SA/Na^{+}REC facilitated the penetration of the dyes into the interlayer space. After careful observation, it can be also sent from Table 1 that the order of the adsorption capacity of SA/Na^{+}REC for the dyes saline is Basic Blue 9 > Basic Blue 3 > Basic Yellow 1 > Basic red GTL > Basic Blue 54. The reason has been attributed to the molecular configuration difference among these dyes (Pathavuth and Punnama, 2009). The molecular size of Blue 9 is relatively small.

4. Conclusions

Crosslinked Sodium alginate/Na^{+}-rectorite intercalated nanocomposite microspheres were prepared in an inverse suspension system. The optimal preparation condition was that the amount of Na^{+}REC was 2 wt%, the amount of kalium persulphate was 8% and the amount of N,N′-methylene bisacrylamide was 0.384%. SEM showed that it is loose products with spherical particulate surface. XRD showed that intercalation is formed between Na^{+}REC and sodium alginate. Compared to sodium alginate and Na^{+}REC, SA/Na^{+}REC composite microspheres has higher adsorption capacity for basic cationic dyes.

In this paper, sodium alginate is intercalated into the interlayers of Na^{+}REC and crosslinked by N,N′-methylene bisacrylamide to prepare crosslinked SA/Na^{+}REC intercalated nano-composite microspheres. The studies are very important for further increasing added value of rectorite, enriching basic theory of clay modifying polymer and study on degradable sorbent.

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